

Refining Technologies

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Conventional FCC to maximum propylene production

Fluid catalytic cracking (FCC) is one of the most important conversion processes used in refineries. This process converts heavy petroleum fractions into lighter, higher-value products, such as gasoline, propylene and others. FCC units (FCCUs) have the flexibility to process a wide range of feedstocks, and at varying severities, to optimize refinery profitability. Maximization of propylene production from FCCUs has become a means for refiners to maintain their competitiveness. This article provides insight into an advanced propylene maximization catalytic cracking (PMCC) technology^a that integrates process, hardware and catalyst. The technology's propylene yield is higher than any other FCC technology, providing an increased operating margin (product revenues minus feedstock costs) of as much as \$2.60/bbl over traditional operations. The key value drivers of this cutting-edge technology are discussed here, along with an overview on global propylene demand and its greater price stability, which are providing an incentive for refiners to shift from fuels production to petrochemicals.

The FCC process. Accounting for approximately 30% of the total crude processed, the FCC process is at the heart of the modern petroleum refinery. FCCUs hold a strong market share, with a processing throughput of around 5 MMbpd in the U.S. and 18 MMbpd worldwide. The conventional FCC process was developed primarily to produce high-octane gasoline from vacuum gasoil (VGO) feedstocks. However, with decreasing gasoline demand growth, forward-looking refiners are exploring new revenue options and shifting to petrochemical-oriented operations.¹ FCCUs are poised to undergo a transition to maximize existing asset utilization and boost profitability.

Market assessment. The demand for transportation fuels is forecast to slow down, primarily due to increased vehicle fuel efficiency, the adoption of electric vehicles and demographic/lifestyle changes. Furthermore, the COVID-19 pandemic has had an unprecedented impact on fuel demands, causing refineries to either operate at reduced throughput or to move forward with their turnarounds to perform maintenance activities. In April, stay-at-home measures in the U.S. resulted in a drastic decrease in gasoline demand of approximately 3.75 MMbpd, which corresponded to a 40% decline in demand vs. the previous year (FIG. 1).

Comparatively, the decrease in propylene demand during the same period was much lower—only 10% vs. the previous year—and the rest of 2020 is forecast to be flat vs. 2019 levels,

based on data from IHS Markit.² This is primarily due to a substantial increase in propylene demand in the personal protection, non-woven, medical and food packaging sectors, which countered decreased demand from the construction and automotive sectors.

Despite the COVID-19 pandemic, the demand for petrochemicals is expected to increase. FIG. 2 shows the projected 5-yr compound annual growth rate (CAGR) for gasoline and propylene for different regions around the world. Gasoline demand is forecast to be flat or slightly negative in North America and Europe, moderate in China and the rest of Asia, and greatest in India. Conversely, propylene demand is forecast to show strong growth, with around 3% CAGR or better across all regions.

The recent market trends and future projections have shown that propylene demand is outpacing both gasoline and ethylene demand. However, current propylene production from steam cracking of light naphtha and other on-purpose routes cannot match the projected demand. At present, more than 30% of the global propylene pool is derived from FCCUs. The historic and projected shifts in propylene production routes are shown in FIG. 3. The predicted shortfall of propylene is growing, presenting a strong incentive to increase FCC propylene yield.

The main drivers for the shifted trend are:

1. A change from naphtha to ethane feedstock, which is reducing the propylene yield from steam crackers

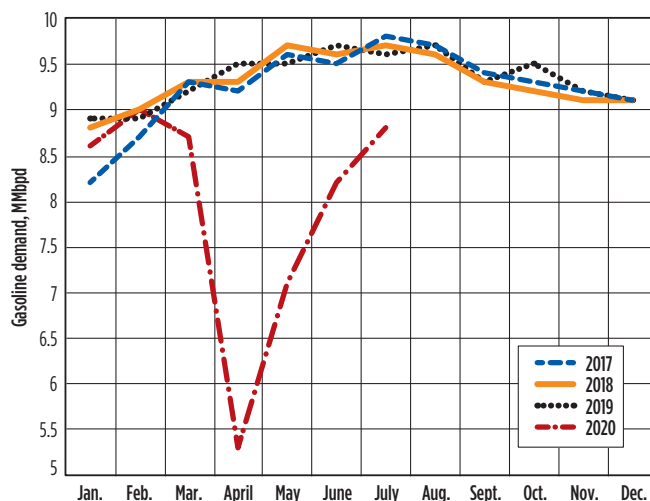


FIG. 1. COVID-19's impact on U.S. gasoline demand. Source: U.S. Energy Information Administration (EIA).

2. A slowdown in demand for transportation fuels, which will temper new refinery and FCC builds.

New grassroots FCCUs are most attractive in markets where there is an increasing demand for both transportation fuels and petrochemicals (e.g., India and Asia). In other markets, where transportation fuel demand is expected to slow but there is positive growth in propylene demand, on-purpose propylene production routes—such as propane dehydrogenation (PDH)—are expected to have positive growth, provided there is long-term availability of propane at a reasonable price.

In these markets, an alternative to on-purpose propylene routes that can be incorporated into existing refining assets are FCCU revamps to increase the propylene yield at the expense of gasoline. The slowing demand for transportation fuels will challenge the financial viability of refineries. By shifting focus to petrochemical production, increasing the yield of petrochemicals from crude, and then integrating with assets to further derive value from petrochemicals, refineries can position themselves to remain viable.

High-propylene-producing FCC technology. The novel PMCC process^a is the newest generation of highly successful, high-olefins-cracking technology that has been further developed for greater feed flexibility and higher propylene yield than the current industry standards. To achieve a high yield of propylene, it is important to set the proper operating conditions,

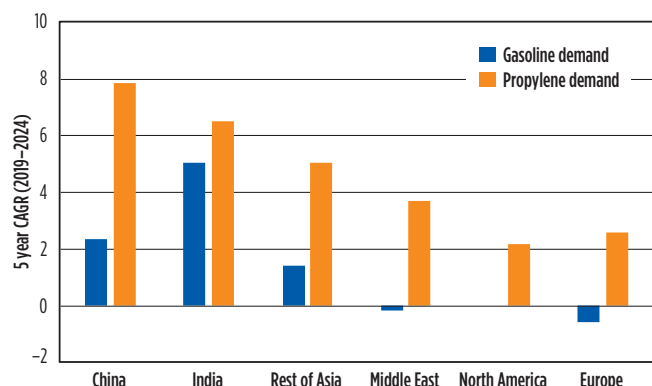


FIG. 2. Forecast for global gasoline and propylene demand, 2019–2024. Source: Wood Mackenzie (gasoline data), ICIS (propylene data).

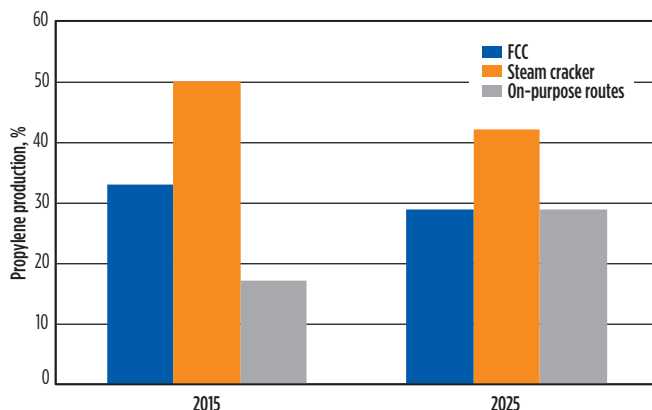


FIG. 3. Global trend of propylene production by route. Source: ICIS.³

to have the right equipment, and to use a catalyst that can deliver the conversion and propylene selectivity required. This technology provides a synergistic integration of these three key pillars—process conditions, catalyst and hardware configuration—to achieve the maximum propylene yield.

Details on these pillars include:

- **Process conditions**
 - Higher-severity operation: Higher reactor temperature and increased catalyst-to-oil ratio
 - Lower hydrocarbon partial pressure: Optimized steam rates and lower reactor pressure
 - Potential to recycle C_4 s, light cracked naphtha (LCN) and oligomer to maximize propylene
- **Proprietary high-propylene catalyst**
 - Optimum catalyst pore structure for fastest diffusion of reactants and products into and out of the catalyst for minimum hydrogen transfer
 - Metals traps to limit destruction of the zeolite by vanadium (V) and nickel (Ni) passivation to reduce hydrogen and coke make at high Ni levels
 - Highest-activity ZSM-5 additive for maximum cracking of gasoline olefins into propylene
- **Hardware configuration**
 - Riser and bed cracking: Optimum weight hourly space velocity (WHSV) to convert naphtha to propylene and optional bed cracking to boost ethylene, along with high propylene
 - Single- or two-stage regeneration, depending on feedstock and unit heat balance: Two-stage catalyst regeneration to handle residue feed with high metals and Conradson Carbon residue (CCR), as well as a compact design
 - Optional separate second riser for selective cracking of recycled LCN stream
 - Robust and reliable proprietary components, providing optimum process performance.

These three building pillars of PMCC—process conditions, catalyst and hardware configuration—can be tailored to meet industry demand of high ethylene or gasoline with propylene.

Configuration. The PMCC technology's reactor generally operates in two reaction modes: Mode 1, with all riser cracking aimed to achieve high propylene and gasoline production; and Mode 2, with bed-cracking targets of high-propylene and ethylene production and relatively low gasoline production. The mode of operation can easily be switched during the operation by changing the bed height in the reactor, with respect to the riser termination device. The technology's configuration (**FIG. 4**) provides a general schematic of the reactor configuration with two-stage regeneration, specifically for processing heavier feedstocks.

Bed cracking is a key aspect of the technology, contributing additional propylene yield to an overall olefin pool. The product vapors from the riser undergo further cracking in the bed to convert naphtha vapors to propylene-enriched LPG. A good distribution of hydrocarbon vapor into the reactor bed is achieved with a proprietary “mushroom distributor” riser termination device, which ensures enough residence time for those vapors in the bed to further crack and promote olefins yield, particularly propylene and ethylene.

Single- or two-stage regeneration depends on the feed type. Single-stage regeneration is generally used for processing VGO feedstocks with CCR of less than 3 wt%; whereas, two-stage regeneration is used for high metals residue feedstocks.

The two-stage regenerators operate at much milder conditions for catalyst regeneration, with the first-stage regenerator operating in partial burn mode followed by full burn mode in the second-stage regenerator. This approach is different from other two-stage commercial designs and results in a fully regenerated catalyst, with the lowest possible regeneration temperatures through the rejection of carbon monoxide (CO)-enriched flue gas from the first-stage regenerator. This ensures the highest possible catalyst-to-oil ratio for a given riser outlet temperature (ROT), as required to maximize olefin yields. The first-stage regenerator operates at lower temperatures and an oxygen-deficient environment, while the second-stage regenerator operates at high temperatures and in a moisture-deficient environment. Since most of the coke hydrogen is combusted in the first stage, the potential for high-temperature hydrothermal catalyst deactivation is minimized in both regenerators, significantly reducing the catalyst makeup rates.

The two-stage regeneration has an inherent built-in catalyst cooler feature, as it rejects the heat as CO from the first-stage regenerator flue gas. This configuration generally reduces and, in many cases, eliminates the need for a catalyst cooler for heavy feeds with a CCR of 3 wt%–5 wt%, depending on the cracking severity. The key attributes of two-stage regeneration are:

- Two smaller vessels that allow for higher-capacity units without requiring one large regenerator
- A compact design and smaller footprint
- Maintains catalyst activity and lowers the catalyst makeup rate
- Smaller catalyst inventory
- Less catalyst cooler duty required
- Lower utility requirement.

A dedicated LCN riser is another important key feature to boost propylene yield. Processing LCN in a separate riser allows for the preferential cracking of olefins, which would be less effective if LCN is fed to a main riser with the fresh feed. In the main riser, ZSM-5 additive easily cracks C_7 – C_{10} olefins to LPG, compared to the more difficult-to-crack C_5 and C_6 olefin components. Processing LCN in a separate riser provides the flexibility to increase the cracking severity to meet the desired catalyst-to-oil ratio, temperatures and the residence time required to crack these components and attain higher propylene yield. The use of a separate riser for LCN processing is generally determined based on feed quality and processing targets, keeping in mind the additional investment vs. the gain in overall profitability.

High-propylene catalyst. A salient feature of the technology is the use of a proprietary high-propylene catalyst^b that is designed to work seamlessly within the cracking environment. While maximizing propylene is a key objective, each refinery is different in terms of configuration of unit operations, crude diet and product values. The catalyst is designed to aid a refiner with minimizing crude and operating expenses, while maximizing the value of all products and throughput. The catalyst for a high-propylene-producing FCCU is formulated, considering the following aspects:

- Unit feed type: Resid and/or VGO
- Desired product yield slates
- Unit constraints, such as the maximum regenerator temperature or maximum catalyst circulation, among others.

In general, to maximize propylene and the FCC gasoline research octane number (RON), the selected catalyst generates and preserves the maximum yield of gasoline-range olefins so that these can be further cracked by ZSM-5 additive into propylene. The concept is illustrated in **FIG. 5**, showing the catalytic approach to maximizing LPG olefins from the FCCU.

The three key aspects of catalyst design are:

1. **Optimum catalyst pore structure designed for high diffusivity of reactant and product molecules:** By facilitating the diffusion of products and reactants into and out of the catalyst, hydrogen transfer is minimized; therefore, gasoline olefins are preserved for subsequent cracking by ZSM-5 additive.

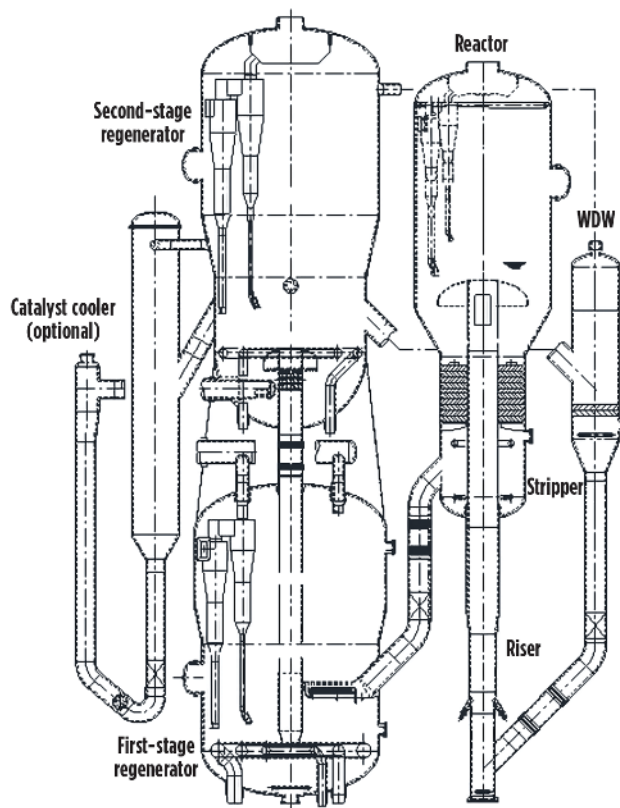


FIG. 4. The PMCC process configuration with two-stage regeneration for heavier residual feedstocks.

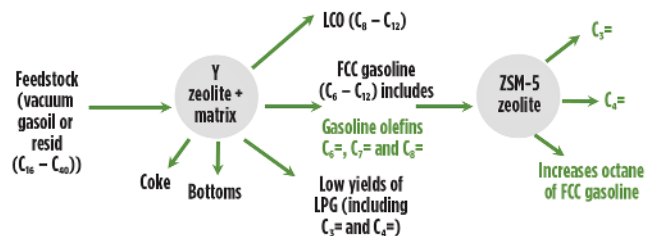


FIG. 5. High-propylene catalyst fundamentals.

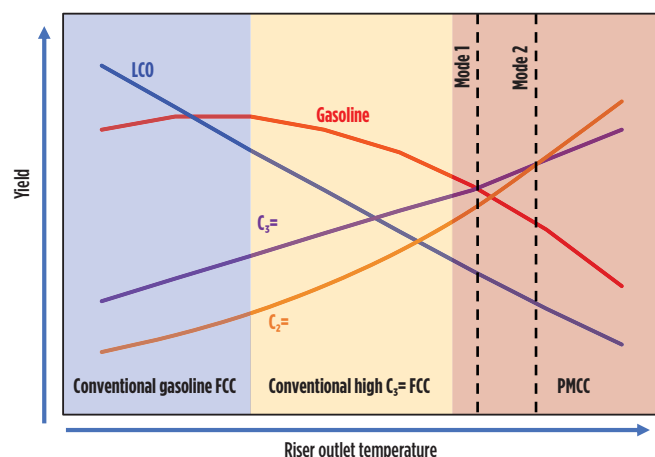


FIG. 6. Impact of ROT on FCC yields.

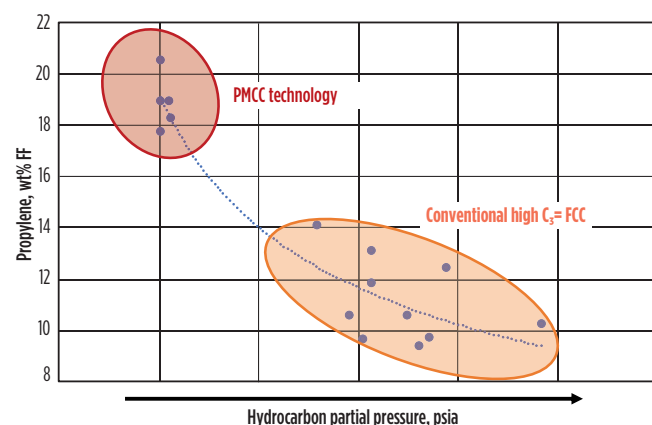


FIG. 7. Impact of hydrocarbon (HC) partial pressure on propylene: The PMCC technology^a vs. other high-propylene FCCU technologies.

- 2. Metals trapping for activity retention and coke selectivity:** Applications seeking to maximize LPG olefins from residue feedstock are more challenging vs. VGO because residue are usually lower in hydrogen content, thereby limiting conversion and propylene potential from the feed. They also contain high levels of V and Ni contaminant metals. V promotes Y zeolite destruction, especially in the presence of sodium, and Ni promotes dehydrogenation and coking reactions. V-traps can be incorporated into the catalyst to limit the destruction of the zeolite, thereby preserving activity. Ni traps can be incorporated to reduce hydrogen yield and improve coke selectivity at elevated Ni levels on the equilibrium catalyst, increasing product value. High CCR levels in the residue feedstock increase delta coke, reducing catalyst circulation. This requires catalyst and equipment technologies that provide superior coke selectivity and low delta coke to ensure high conversion and propylene selectivity.
- 3. Maximum-activity ZSM-5 additives:** Due to high-propylene-yield targets, an optimum addition rate of ZSM-5 additive is needed. Since ZSM-5 additive

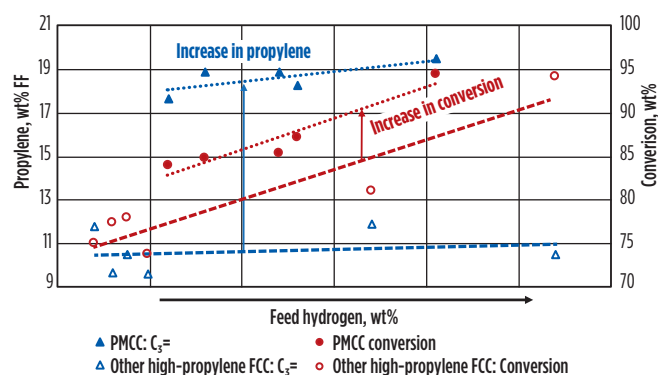


FIG. 8. Propylene and conversion vs. feed hydrogen: PMCC technology^a vs. other high-propylene FCCUs.

primarily cracks gasoline-range molecules, adding a high level of ZSM-5 additive results in the dilution of the Y-zeolite base catalyst activity, which is essential for cracking the larger molecules. The main benefit of using the highest-activity ZSM-5 additive vs. the use of a lower-activity ZSM-5 additive is to minimize the dilution of the base catalyst activity.

Process conditions. The PMCC technology's reactor/regenerator configuration provides an ample opportunity to tune the process variables in conjunction with the catalyst to achieve the desired yield slates. High-severity operation and low-hydrocarbon partial pressure are the key variables favoring propylene.

High-severity operation is generally achieved by combining high ROT and a high catalyst-to-oil ratio. The impact of ROT on yields is well depicted in FIG. 6, showing how the operating windows shift from traditional gasoline-oriented FCC to the PMCC technology's Mode 1 and Mode 2 operations. Compared to conventional gasoline or high-propylene FCC, the PMCC process operates at a higher ROT, resulting in yield shifts toward the lighter components. Gasoline-range material is cracked to LPG and lighter products, and the traditional LCO cut is cracked to gasoline. Mode 2 operates at higher severity with bed cracking to target high yields of ethylene and propylene at the expense of gasoline, whereas Mode 1 targets comparatively lower ethylene.

Low reactor pressure and high steam usage. In FCC cracking reactions, a low hydrocarbon partial pressure is key for promoting secondary naphtha cracking and achieving high propylene yield in concert with the low-hydrogen-transfer proprietary catalyst technology.^b Low hydrocarbon partial pressure not only favors propylene formation, but also retards the hydrogen transfer reactions that saturate olefins (e.g., converting propylene to propane). This is generally achieved by operating the reactor at the optimum combination of lower pressure and higher steam rate compared to a typical FCCU. The incremental gain in propylene yield with the PMCC technology operating at low partial pressure has been commercially demonstrated multiple times. FIG. 7 shows an industrial survey of 15 high-propylene commercial units. Five are PMCC units operating at lower partial pressure. The units collectively produce the highest propylene yield on a sustained basis over sev-

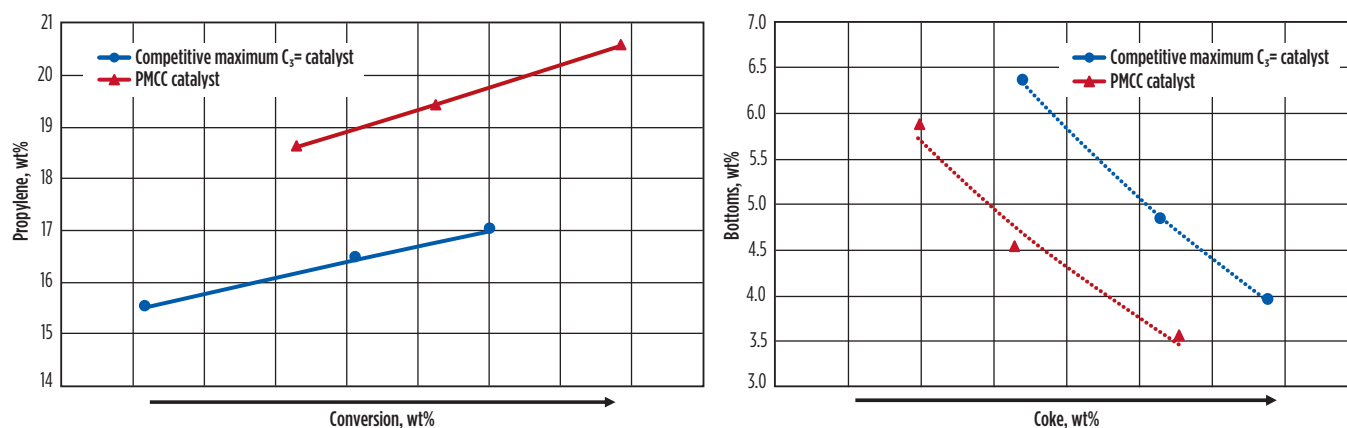


FIG. 9. Performance comparison of the PMCC technology's catalyst vs. competitive maximum-propylene catalyst.

eral years, showing a clear advantage over other high-propylene FCC technologies available in the industry.

Feedstock properties are an important consideration in determining the full potential for propylene yield from a given feedstock. Hydrogen content—a key feed parameter—is a primary indicator of feed crackability. For example, a more aromatic feedstock typically has low hydrogen content and is difficult to crack in an FCCU, whereas a more paraffinic feed has higher hydrogen content and is easier to crack to lighter components. The feed hydrogen content typically correlates well with the unit conversion and propylene yield (FIG. 8), depending on the technology type. FIG. 8 shows the propylene yield and conversion from commercial units as a function of feed hydrogen. The PMCC technology features enable it to achieve 60%–80% higher propylene for the same feed quality compared to conventional high-propylene FCCUs. The conversion achieved in these units is also considerably higher, emphasizing the influence of technology type on maximizing the product value.

Competitiveness of the technology's catalyst. Through continuous innovation, significant advancements to the technology's catalyst offerings have been made. These advancements provide optimum catalytic activity and the highest propylene production, in addition to the desired product selectivity to maximize refinery profitability. The offered catalyst is proven in the industry to provide the best propylene yield possible under PMCC conditions. A comparison between the PMCC technology's catalyst and a commercially competitive maximum propylene catalyst is shown in FIG. 9. As indicated, the PMCC technology catalyst shows higher propylene selectivity than the competitive catalyst at the same conversion level. Using this catalyst, the propylene yield exceeds 19 wt%, which is nearly 3 wt% higher than the competitive catalyst. In addition, PMCC catalyst produces lower coke and less slurry. This comparison clearly indicates that high-propylene catalyst technology provides an optimum integration with the PMCC technology process and hardware.

Feed flexibility: VGO to resid. The process variables, catalyst selection strategy and hardware configuration for the PMCC process are well optimized to provide the flexibility to process a wide range of feedstocks, as well as to maximize pro-

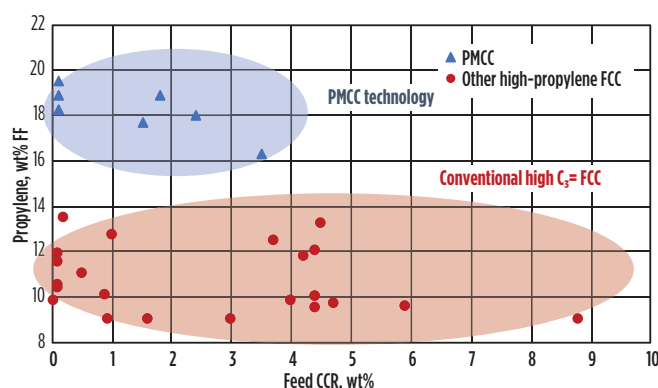


FIG. 10. Commercial C_3 vs. feed CCR: PMCC technology vs. conventional high-propylene FCCU.

pylene yield within the unit constraints. The propylene yields from various commercial units processing different feedstocks (FIG. 10) clearly show the advantage of the PMCC process technology for propylene production compared to conventional high-propylene FCCUs.

The ex-reactor propylene yield is plotted as a function of feed CCR for several commercial units in FIG. 10. As shown, propylene yields of 12 wt%–14 wt% can be achieved at feed CCRs up to ~5 wt% with conventional high-propylene FCCUs—whereas, more than 18 wt% propylene yield can be achieved with the PMCC process at feed CCRs as high as 3 wt%. The PMCC process delivers a higher propylene yield at similar feed CCRs vs. other high-propylene FCC technologies. High yields of the PMCC process are not limited to hydrotreated VGO but can also be achieved by processing hydrotreated residue feeds.

Yield selectivity. Understanding the significance of catalyst cracking technologies and their quantitative impact on fuels to petrochemical potential plays a key role in deciding future investment opportunities for both grassroots applications and for revamps of existing assets. The change in yield selectivity based on different FCC technologies on the same feed basis (FIG. 11) highlights the benefits of the PMCC process in delivering increased yields of high-value products. The comparison clearly shows that the technology brings higher operating margins

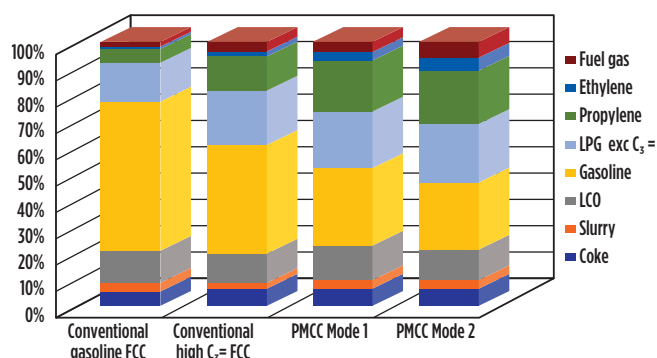


FIG. 11. Yield comparisons of the PMCC process vs. others.

(product revenues minus feed cost) to the refiner, equivalent to \$1/bbl for Mode 1 or \$2.60/bbl for Mode 2 over a conventional gasoline FCCU. The analysis was conducted considering 2020 Southeast Asian product and crude pricing. Integrating the PMCC process in the refinery scheme, or converting an existing FCCU to the technology, helps bridge the propylene demand/supply gap and boost refinery profitability.

A refinery integrated with the PMCC technology can contribute 10 wt%–12 wt% to chemicals from each barrel of crude, with up to 7 wt% propylene per unit of crude processed. This technology is one of the key pillars for an integrated refinery and petrochemical complex targeting higher production of crude-to-chemicals for both grassroots facilities and for the upgrade of existing complexes.⁴

Takeaways. Market trends suggest that propylene demand will continue to increase, while demand growth for transportation fuels will slow. An opportunity exists for refiners who have previously targeted primarily gasoline and diesel production to upgrade their existing FCCUs to produce more propylene and to capture the growing demand to remain financially viable into the future. Maximum propylene production from the FCCU has been the primary focus of many refiners, primarily in Asia, Europe and the Middle East. Compared to a traditional gasoline FCC operation, the PMCC process can bring additional product values (e.g., as much as \$2.60/bbl).

Whether refiners are planning for a grassroots unit or revamping their existing unit to maximize their revenues through increased propylene production, the key concern is to maintain the flexibility to switch their operation between propylene and gasoline when needed to cope with changing market demands. The PMCC process offers a commercially proven design for achieving high propylene yield, along with the operational flexibility to switch from maximum propylene mode to maximum fuel mode while in operation.

This technology provides a synergistic integration of three key pillars (process conditions, catalyst and hardware configuration) to achieve maximum propylene yield. The technology's reactor regenerator configuration can be easily tailored with a single or dual riser and with single- or two-stage regeneration to provide flexibility in processing different feeds, as well as to meet different product requirement targets. Furthermore, the authors' companies can customize the operating conditions and catalyst to maximize propylene yields and other key products to

align with the refinery configuration and crude slate to deliver increased profits to the refiner.

The three key aspects of catalyst design are optimum catalyst pore structure, advanced metals trapping technology for activity retention and coke selectivity, and maximum-activity ZSM-5 zeolites. This technology collaboration brings immense experience in the field of light olefins FCC and ensures continuous development of innovative solutions to meet refining needs. **HP**

NOTES

^a Refers to TechnipFMC's PropyleneMax™ catalytic cracking technology (PMcc™)

^b Refers to W. R. Grace's VIP-R™ high-propylene catalyst

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